### **California Environmental Protection Agency**

# Air Resources Board

PROCEDURE FOR THE DETERMINATION OF BENZENE, TOLUENE, ETHYLBENZENE, P/M-XYLENE, O-XYLENE, C9 AND HEAVIER AROMATICS AND TOTAL AROMATICS IN GASOLINE BY GAS CHROMATOGRAPHY

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#### 1 Introduction

- 1.1 This document describes an automated method of analyzing benzene, toluene, ethylbenzene, the xylenes, aromatic hydrocarbons with nine or more carbons (C9 and heavier aromatics), and total aromatics in gasoline by gas chromatography.
- 1.2 This test method requires two separate analyses in order to determine the total aromatic content of gasoline. The first analysis is used to quantitate benzene and toluene. The second analysis is used to quantitate ethylbenzene, p/m-xylene, o-xylene, and the C9 and heavier aromatics. The results of both analyses are summed to determine the total aromatic content.
- 1.3 This test method covers the following concentration ranges, in liquid volume percent, for the aromatics listed above: benzene, 0.1 to 5%; toluene, 1 to 15%; individual C8 aromatics (ethylbenzene, o-xylene, m-xylene, p-xylene), 0.5 to 10%; total C9 and heavier aromatics, 5 to 30%; and total aromatics, 10 to 80%.
- 1.4 Nonaromatic hydrocarbons having a boiling point higher than that of n-dodecane may cause interferences with the determination of C9 and heavier aromatics. There are no other known interferences.
- 1.5 This procedure is based on ASTM D5580-95<sup>1</sup>.

### 2 Method

- 2.1 Gasoline samples are collected and brought to the laboratory where an internal standard, 2-hexanone, is added volumetrically to the samples prior to analysis.
- 2.2 A two-column gas chromatographic system equipped with a column switching valve is used. Two analyses are performed. The first analysis is used to speciate benzene and toluene. The second analysis is used to speciate the C8 aromatics and to determine the C9 and heavier aromatics.
- 2.3 For the first analysis, an autosampler injects a known volume of sample onto a packed precolumn containing a polar liquid phase (TCEP). The C9 and lighter nonaromatics are vented to a second detector as they elute from the precolumn. The precolumn is backflushed immediately before the elution of benzene, and the remaining portion of the sample is directed onto a second capillary column (WCOT) containing a nonpolar liquid phase (DB-1). Benzene,

toluene, and 2-hexanone elute and are detected by a flame ionization detector (FID). Immediately after the elution of the 2-hexanone, the flow through the WCOT column is reversed to backflush the remainder of the sample (C8 and heavier aromatics plus C10 and heavier nonaromatics) from the column to the flame ionization detector.

- 2.4 The analysis is repeated in order to quantitate the C8 and heavier aromatics allowing the C12 and lighter nonaromatics, benzene, and toluene to elute from the polar TCEP precolumn to vent. The precolumn is backflushed immediately prior to the elution of ethylbenzene and the remaining aromatic portion is directed into the WCOT column. 2-Hexanone and the C8 aromatic components elute in the order of their boiling points and are detected by an FID. Immediately after o-xylene has eluted, the flow through the WCOT column is reversed to backflush the C9 and heavier aromatics to the flame ionization detector.
- 2.5 The data system identifies the aromatic compound associated with each chromatographic peak. The FID response, proportional to the concentration of each component, is used to calculate the amount of aromatics that are present by comparison with the internal standard.

#### 3 Instrumentation

- 3.1 Gas chromatograph: Varian model 3800 or Hewlett-Packard model 6890 equipped with 2 FIDs.
- 3.2 Columns
- 3.2.1 The following columns are connected to the gas chromatograph as shown in Figure 1:
- 3.2.2 Polar precolumn: any column with chromatographic efficiency and selectivity equivalent or better than: 560 mm by 1.6 mm outside diameter by 0.38 mm inside diameter stainless steel tube packed with 0.14 to 0.15 g of 20% 1,2,3,-tris-2-cyanoethoxypropane (TCEP) on 80/100 mesh chromasorb P(AW).
- 3.2.3 Nonpolar analytical column: 30 m long by 0.53 mm inside diameter fused silica wall-coated open tubing (WCOT) column with a 5.0 micrometer film thickness of cross-linked methyl siloxane (J&W DB-1 or equivalent).
- 3.3 Liquid autosampler: Varian model 8400 or Hewlett-Packard model 6890.
- 3.4 Digital data acquisition system: Varian Star or Hewlett-Packard Chemstation.

### 4 Reagents

- 4.1 Benzene, toluene, ethylbenzene, o-xylene, p/m-xylene, 1,2,4-trimethylbenzene, 2,2,4-trimethylpentane (isooctane), n-dodecane, American Chemical Society (ACS) reagent grade or equivalent
- 4.2 2-Hexanone, 98% Aldrich or equivalent
- 4.3 Air, Zero grade
- 4.4 Nitrogen, 99.998%
- 4.5 Helium, 99.995%
- 4.6 Hydrogen, 99.995%
- 4.7 Calibration standards are prepared every year as follows: Prepare multi-component calibration standards containing benzene, toluene, ethylbenzene, o-xylene, and 1,2,4-trimethylbenzene at the concentrations given below. O-Xylene is used to represent the xylenes and 1,2,4trimethylbenzene is used for the C9 and heavier aromatics. For benzene, concentrations of 0.1, 0.5, 1.0, 2.0, and 5.0 volume % can be used. For toluene, the concentrations are 1.0, 2.5, 5.0, 10.0, and 15.0 volume %. For the other components, the concentrations are 0.5, 1.0, 2.5, 5.0, and 10.0 volume %. The samples are prepared using an analytical balance and that mass percentages are used with the data acquisition software. Prepare standards by transferring a fixed volume of aromatic component using pipettes to a 100 mL volumetric flask. Cap and record the tare weight of the flask to 0.1 mg. Remove the cap and add the aromatic components to the flask starting with the least volatile (1,2,4-trimethylbenzene), capping and weighing the flask after each addition. Do not exceed 50 volume % for all aromatics added. Similarly, add 10 mL of 2-hexanone and record its mass to the nearest 0.1 mg. Dilute each standard to the mark with isooctane. Store the calibration standards in a refrigerator at 0 to 5 °C when not in use.

### **5** Preparation of Instrument

- 5.1 The operating conditions are set to those listed in Table 1. The column temperature is set to 60 °C.
- 5.2 Flow Rate Adjustments

- 5.2.1 Attach a flow measuring device to detector A (the detector on the precolumn). With the valve in the RESET or forward flow position, adjust the pressure of the capillary injection port (figure 1) to give a 10.0 mL/min flow.
- 5.2.2 Attach a flow measuring device to the split injector vent and adjust the flow controller to give a flow of 100 mL/min. Recheck the column vent flow set in 5.3.1 and adjust if necessary. The split ratio should be approximately 11:1.
- 5.2.3 Switch the valve to the BACKFLUSH position and adjust the variable restrictor to give the same precolumn vent flow set in Section 5.3.1. This is necessary to minimize flow changes when the valve is switched.
- 5.2.4 Switch the valve to the RESET position and adjust the auxiliary flow controller to give a flow of 10 mL/min at the detector B (analytical column) exit.
- 5.2.5 Set the nitrogen makeup flow to 20 mL/min, the hydrogen flow to 30 mL/min, and the air flow to 300 mL/min.
- 5.3 Valve Timing
- 5.3.1 Set the valve to RESET and inject a blend containing benzene, ethylbenzene, o-xylene, and 2-hexanone in isooctane. Alternatively, the calibration mixture described in 4.7 can be used instead. Determine the retention time at which benzene and ethylbenzene start to elute as measured by detector A. Subtract 0.05 minutes from these times and call them T1 and T2 respectively. See Figure 2.
- 5.3.2 Re-inject the blend and turn the valve to BACKFLUSH at time T1. When the 2-hexanone peak on detector B returns to the baseline, switch the valve back to RESET. Call this time T3. See Figure 3.
- 5.3.3 Re-inject the blend and turn the valve to BACKFLUSH at time T2. When the o-xylene peak on detector B returns to the baseline, switch the valve back to RESET. Call this time T4. See Figure 4.
- 5.4 Polar Precolumn Sensitivity Check
- 5.4.1 Prepare a blend containing approximately 1.5% n-dodecane in isooctane. Inject 1.0 µL of the mixture under the conditions given in 5.2-5.3 and actuate the valve at time T2 (BACKFLUSH) and time T4 (RESET). Verify that n-dodecane fully elutes from the polar precolumn (detector

- A) before time T2. If not, part of the n-dodecane peak will be backflushed to the nonpolar WCOT column and be detected by detector B after time T4.
- 5.4.2 If all of the n-dodecane peak is not completely vented from the polar precolumn, recheck the instrument parameters and valve backflush times or replace the polar precolumn. If the valve and precolumn are contained in a separate heated zone it may be necessary to raise the temperature of the zone.

#### 6 Calibration

- 6.1 Calibration must be performed whenever significant adjustments or repairs are performed on the instrument (e.g. column replacement) or when the instrument repeatedly fails its quality control criteria (see Section 10). Additionally, calibration is performed whenever a new set of calibration standards is made.
- 6.2 With the valve initially in the RESET position, chromatograph each of the calibration mixtures twice using the valve timing procedures described above. For the first analysis use times T1 and T3. For the second analysis use times T2 and T4.
- 6.3 The data acquisition software with automatically generate calibration curves and calculate an r<sup>2</sup> value. If this value is less than 0.990, the calibration must be rerun or the instrument parameters and hardware checked.
- Y-intercept test: For an optimum calibration, the absolute value of the y-intercept must be at a minimum. The y-intercept for each component's calibration can be tested using the equation below:

$$t_i = (b_i / m_i)(W_s / W_g)100\%$$

where  $b_i$  is the y-intercept for the aromatic component in question from the calibration equation,  $m_i$  is the slope of the calibration line,  $W_s$  is the mass in grams of internal standard added, and  $W_g$  is the mass in grams of the calibration mixture. For benzene,  $t_i$  must be less than 0.02 mass %. For the other components,  $t_i$  must be less than 0.2 mass %. If any of the  $t_i$  values exceeds the limit, the calibration must be rerun.

#### 7 Procedure

- 7.1 Transfer 1 mL of 2-hexanone by a volumetric pipette into a tared and capped 10 mL volumetric flask. Record the net mass of internal standard to 0.1 mg. Retare the flask and fill to the mark with sample. Cap the flask and record the net mass of sample added to 0.1 mg. Mix thoroughly. Transfer an appropriate amount of the mixture to a glass autosampler vial.
- 7.1.1 Repeat step 7.1 for each sample.
- 7.2 A 1.0 µL aliquot of each sample is injected via autosampler into the gas chromatograph under the same conditions used for the calibration samples. Each sample is chromatographed twice, once using T1 and T3 and once using T2 and T4 for valve timing.
- 7.3 A control standard is analyzed at the beginning and at the end of each set of samples.
- 7.4 Peak identifications provided by the data system are check and corrected, if necessary. See Figures 3 and 4 for sample chromatograms.

### 8 Safety

8.1 All chemical compounds used in this method are flammable. Aromatic compounds are toxic and benzene is a known carcinogen. Persons using this method must use a fume hood with adequate ventilation and wear protective gloves and eyewear while working with reagents and samples.

#### 9 Calculations

9.1 The mass of each aromatic component in the sample is determined by the following equation:

$$W_i = (((A_i / A_s) - b_i) / m_i) W_s$$

where  $W_i$  is the mass of aromatic component I,  $A_i$  is the area of the peak corresponding to aromatic component I,  $A_s$  is the area of the 2-hexanone peak,  $W_s$  is the mass of 2-hexanone added, and  $m_i$  and  $b_i$  are the slope and intercept of the calibration curve for aromatic component I determined in Section 6.3.

9.2 The mass % of each aromatic component is determined by the following equation:

$$w_i = 100(W_i / W_g)$$

where  $w_i$  is the mass % of aromatic component I,  $W_i$  is the mass of aromatic component I determined in Section 9.1, and  $W_g$  is the mass of the gasoline sample. Total aromatic concentration is obtained by adding the mass % values of each aromatic component.

9.3 The volume % of each aromatic component is determined by the following equation:

$$v_i = w_i (D_f / D_i)$$

Where  $v_i$  is the volume % of aromatic component I,  $w_i$  is the mass % of aromatic component I determined in Section 9.2,  $D_f$  is the density of the gasoline, and  $D_i$  is the density of aromatic component I as given in table 2. Total aromatic volume % is obtained by adding the  $v_i$  values for all of the aromatic components.

### **10** Quality Control

- 10.1 A blank sample (isooctane) is analyzed after each new calibration set. If the blank chromatogram shows a peak in the region of any of the aromatic components, the blank is repeated or the instrument hardware is checked. All aromatic concentrations must be below the limit of detection before the analysis may proceed.
- 10.2 A control standard is prepared at least once per year using known amounts of eight aromatics. Suggested compounds are benzene, toluene, ethylbenzene, p-xylene, o-xylene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and napthalene. The control is analyzed at the beginning and at the end of each set of samples.
- 10.3 The analyses of the control standard are recorded on quality control charts. Separate charts are maintained for benzene and total aromatics. A result is considered to be out of control if its difference from the known value is greater than twice the value of the repeatability (see Section 10.5). In this event, corrective action must be taken prior to analyzing samples. If any major repairs are performed on the instrument, it must be recalibrated.
- 10.4 At least once per quarter, NIST Standard Reference Material 2294 must be analyzed for benzene and total aromatics. The values determined must agree with those provided by NIST within the reproducibility of the method (see Section 10.6), or corrective action must be taken.
- 10.5 For benzene measurements, the repeatability is given by the following equation:

$$r = 0.0265(X)^{0.65}$$

where r is the repeatability and X is the measured benzene concentration in mass %. For total aromatics measurements, the repeatability is 0.46 mass %.

10.6 For benzene measurements, the reproducibility is given by the following equation:

$$R = 0.1229(X)^{0.65}$$

where R is the reproducibility and X is the measured benzene concentration in mass %. For total aromatics measurements, the reproducibility is 1.59 mass %.

10.7 Limits of detection (LODs) are determined by the intercept test as discussed in section 6.4.

#### 11 References

1. ASTM D5580-95, AStandard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-xylene, C9 and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography, 1996 Annual Book of ASTM Standards, v. 05.03.

### 12 Revision History

Revision 2.2 Effective Date: January 1, 2003

Table 1

Typical Chromatographic Operating Parameters

Temperatures	
Injection port	200 °C
FID detector A	250 °C
FID detector B	250 °C
Nonpolar column (oven)	
Initial	60 °C (6 minute hold)
Rate	2 °C/min
Final	115 °C (Hold as necessary for elution)
Polar TCEP precolumn	80 °C (if a separate zone is available)
Valve	>115 °C(if a separate zone is available)
Flows and Conditions	
Carrier gas	helium
Flow to TCEP column	10 mL/min
Flow to nonpolar column	10 mL/min
Split flow	100 mL/min
Detector gases	as needed
Split ratio	11:1
Sample size	1 μL

Table 2
Densities of Aromatic Components

Component	Density at 60 °F (g/mL)
Benzene	0.8845
Toluene	0.8719
Ethylbenzene	0.8717
p/m-Xylene	0.8679
o-Xylene	0.8848
C9 and heavier aromatics	0.8764